Superconducting phonon spectroscopy using a low-temperature scanning tunneling microscope

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(Received 29 September 1988; accepted for publication 15 December 1988)

We report the first observation of phonon density of states effects in a superconductor using a low-temperature scanning tunneling microscope (STM). The phonon effects were observed using a STM spectroscopy method to measure $dI_{\text{tunneling}}/dV$ vs V for the tunnel junction formed by the Au STM probe and a superconducting Pb sample.

The scanning tunneling microscope (STM), since its invention,[1] has evolved into a sophisticated tool for direct imaging of many surfaces with atomic resolution. More recently, the STM has emerged as a powerful spectroscopic tool with the potential for observation of surface and subsurface electronic properties also with very high spatial resolution. The large field of conventional tunneling spectroscopy on macroscopic tunnel junctions is credited with many fundamental observations. Measurements involving macroscopic tunnel junctions, however, are limited by the spatial averaging over the junction area and potential insulator barrier induced alteration of the system under study. Due to the local nature of the tunnel current in a STM experiment, one can hope to study macroscopically nonideal samples such as polycrystalline thin films and measure properties of fundamental as well as technological importance.

Historically, tunneling spectroscopy has been the most sensitive probe of the superconducting state. Observation of the superconductor energy gap by current-voltage (I-V) spectroscopy using the STM has been reported.[2-4] In this letter we report, for the first time, the application of the STM to the observation of superconductor phonon density of states effects in conductance-voltage (dI/dV-V) spectroscopy. Conductance spectroscopy has been important in the study of superconductors. In the case of a normal metal-insulator-superconductor (NIS) tunnel junction, the normalized conductance as a function of bias voltage, $\sigma(\text{eV}) = G_{ns}(\text{eV})/G_{nn}(\text{eV})$ where G_{ns} and G_{nn} are the tunneling conductance with the S electrode in the superconducting and normal states respectively, is a nearly exact representation of the superconductor excitation density of states. Small structures in the excitation density of states deviating from the predictions of the Bardeen–Cooper–Schrieffer (BCS) theory[5] were first observed by Giaever[6] using conductance-voltage spectroscopy with macroscopic area tunnel junctions. The deviations are strongest in superconductors such as Pb, and were used to establish the validity of the strong coupling modifications of the theory of superconductivity culminating in the theory of Eliashberg.[7] This structure has been shown to arise from the energy dependence of the phonon mediated electron-electron coupling responsible for the superconducting state. The deviations from BCS behavior in Pb observed in conductance-voltage spectroscopy are weak; the phonon structure is resolved as a change in conductance of only a few percent of the total conductance. Therefore, the observation of phonons represents a difficult measurement for low-temperature STM where the tunnel current and conductance signals are reduced by a factor of greater than 10^6 compared to conventional macroscopic area tunnel junctions.

Our STM system has been described previously.[4] The basic design is similar to one used for room-temperature STM studies[8] with modification for use in low-temperature STM of superconductors. For phonon spectroscopy the tunnel voltage range of interest is 0.0–20.0 mV. The need to maintain large tunnel resistances in STM spectroscopy has been discussed previously.[4] Tunneling resistance for these measurements was maintained in the 1×10^7–1×10^9 Ω range. Under these conditions the tunneling currents are typically in the range of 20–2000 pA. Two basic requirements for the feedback and spectroscopy method are (1) small voltage control and (2) direct dI/dV measurement. To meet these requirements techniques used in macroscopic tunneling spectroscopy were employed, two tunnel voltage modulation signals at separate frequencies (f_0 and f_1) are applied simultaneously to the STM tunnel junction. The tip-sample separation control is achieved, using techniques similar to those employed in Ref. 2, by measuring the amplitude of the current signal at the lower frequency f_0 with a lock-in amplifier and maintaining this amplitude at a constant value using a feedback circuit. Using this method, the I-V spectra can be measured by monitoring the tunnel voltage and current without interrupting feedback control. The dI/dV-V spectra were measured using standard analog derivative techniques by phase sensitively detecting the modulated current at the higher modulation frequency f_1 using a second lock-in amplifier. To avoid distortions due to slew rate limitations of the second lock-in, it is important to keep f_0 as low as possible while maintaining stable tunneling. In the experiments reported here $f_0 = 10$–20 Hz. I-V spectra were measured as a function of tunneling resistance and have been shown to be independent of tunneling resistance for resistances of 10^7 Ω or greater. The sweep frequency f_0 was also varied to check for distortions due to insufficient electronic bandwidth. In this regard, the preamplifier incorporated into our STM design is critical. The spectra were acquired by a signal averager to improve the signal to noise ratio.

The superconducting materials were thin films deposited on silicon. The Pb samples were thermally evaporated from 99.999% pure metal in a liquid-nitrogen trapped diffusion-pumped vacuum chamber. The NbN was deposited by reactive dc magnetron sputtering from a high-purity Nb target in an argon-nitrogen atmosphere in a high vacuum chamber under conditions used for making NbN-based tunnel junctions.[9]

A topogram of NbN taken at 4.2 K using the low-temperature STM is shown in Fig. 1. The surface reveals a single-crystal grain with a sequence of two atom layer high steps. Topograms such as this can be rescanned over periods of many hours with minimal drift in the scan window. This stability is required in the derivative spectroscopy experiments where extensive signal averaging is need to enhance the signal-to-noise ratio.

Shown in Fig. 2 is an electron tunneling I-V spectrum for NbN taken with a STM at 4.2 K. The data exhibit NIS character with the characteristic superconductor energy gap clearly defined. The small conductance region followed by a sharp rise in the current at one half the gap voltage and an asymptotic approach to the normal-state tunneling characteristic clearly distinguishes NIS tunneling from other tunneling I-V characteristics. The theoretical I-V data can be numerically calculated using an elementary tunneling formalism and BCS density of states.[10] Using a single parameter Δ and approximating the normal conductance from the data gives $\Delta = 2.58$ meV, which is in the range expected for NbN.[11,12]

An I-V spectra obtained by electron tunneling into Pb at 4.2 K using the low-temperature STM is shown in Fig. 3. The slight hysteresis in the STM spectrum is a result of the bidirectional voltage sweep and the resulting tip-sample displacement current. A fit yields $\Delta = 1.28$ meV for this data. Using the normalized temperature dependence of the energy gap measured by Adler[13] and our fit data at 4.2 K we have

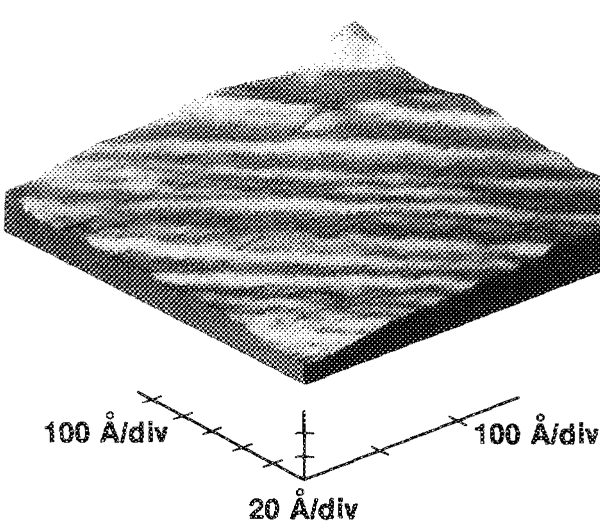

FIG. 1. STM topogram of a sputter-deposited NbN thin film obtained at 4.2 K.

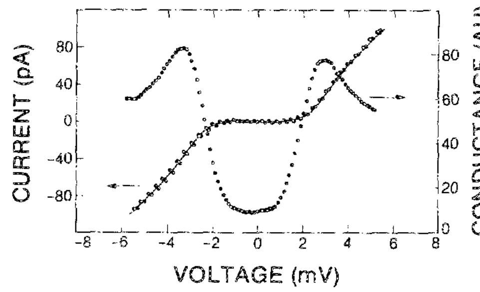

FIG. 2. Electron tunneling current-voltage and conductance-voltage spectra of a NbN thin film measured by STM at 4.2 K. The points are STM data while the line represents a theoretical fit.

calculated a zero temperature gap parameter $\Delta_0 = 1.36$ meV which is within the range observed for Pb.[14] The smaller energy gap of Pb relative to NbN leads to clearly observable changes in the character of this spectrum from that of NbN shown in Fig. 2. The energy gap difference is reflected in the smaller extent of the lower conductance region. In addition, although the subgap current is dominated by the thermal broadening in the normal metal (the energy gap of Pb at 4.2 K is large compared to kT), the extent of the smearing as a fraction of the energy gap leads to a less dramatic I-V nonlinearity.

For NIS tunneling in macroscopic tunnel junctions, the phonon effects occur for voltage bias above one half of the superconductor energy gap and the major structure in the conductance is observed below 13 meV in Pb. It can be seen from the Pb I-V curve in Fig. 3 that the deviations from linearity above the gap are small and derivative spectroscopy is, therefore, required to resolve them. Conductance measurements over the voltage range of interest are shown in Fig. 4 along with that measured using a macroscopic $Pb/AlO_x/Al$ tunnel junction[15] for comparison.[16] There is good qualitative agreement between the experimental STM and macroscopic tunnel junction curves. The conductance-voltage spectra measured by STM covering the superconductor gap voltage range for a NbN thin film are shown in Fig. 2. Phonon density of states effects in NbN are weaker and broader and they were not observed with our STM.

Recently it has been suggested that multiparticle tunneling[17] which is predicted to give rise to excess subgap tunneling current might be operative in STM experiments per-

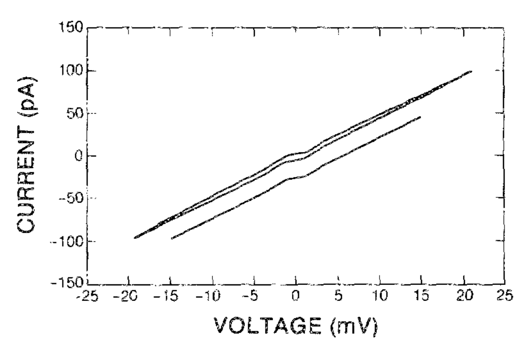

FIG. 3. Electron tunneling I-V spectra of a Pb thin film measuredby STM at 4.2 K (upper curve) and a theoretical fit displaced for clarity (lower curve).

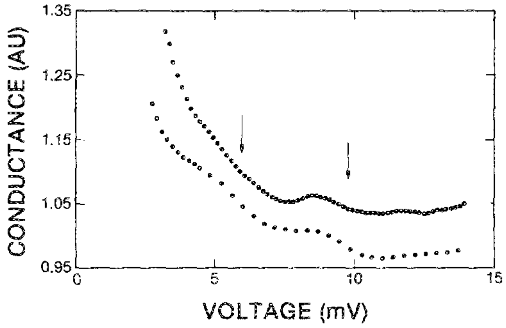

FIG. 4. Tunneling conductance-voltage spectra obtained at 4.2 K for a Pb thin film. The upper curve is measured by STM electron tunneling and the lower measured on a macroscopic $Pb/AlO_x/Al$ tunnel junction. The arrows indicate features associated with the transverse (left arrow) and longitudinal (right arrow) peaks in the phonon density of states.

formed at low tunneling resistance.[18] Careful observation of the *I-V* characteristics in the gap region of NbN did not reveal any excess tunneling current. The BCS-based fit[10] to the NbN *I-V* spectrum in Fig. 2 does not include multiparticle tunneling, yet accounts for the measured subgap currents within experimental error.

In the course of our experiments, we have observed variations in the superconductor energy gap in *I-V* measurements of Pb thin films from region to region on the same sample and from sample to sample. One possible explanation for this observation is the known gap anisotropy of Pb[19] combined with the polycrystalline nature of the deposited films and the local nature of the STM tunnel probe. Experimental zero temperature gap parameter values (Δ_0) reported in the literature for single-crystal samples vary from 1.18 to 1.40 meV.[19] This range includes variations due to direction-dependent gap anisotropy and variations due to multiple energy gap superconductivity arising from different sheets of the Fermi surface. These gap variations are masked in macroscopic tunnel junctions fabricated with polycrystalline films due to spatial averaging, which again highlights the potential of STM to measure fundamental properties on samples which are macroscopically nonideal, such as polycrystalline thin-film samples.

The observation of phonon effects in superconductors represents a measurement of conductance to a minimum of one part in one hundred. This measurement demonstrates that, in principle, variations in phonon effects could be spatially imaged with a STM. However, measurement of low noise spectra with small currents requires extensive signal averaging and limits the spatial resolution with which these variations could be observed in an experiment of reasonable duration. The advantages of STM for conductance spectroscopy may lie in the formation of a microscopic, nearly ideal tunnel junction on samples which are macroscopically nonideal such as polycrystalline thin films. Thus local properties of samples can be measured at selected points of the sample surface.

In summary, we have developed techniques for simultaneous tip-sample separation control and *I-V* and *dI/dV-V* measurement. Using these techniques we have made the first observation of phonon density of states spectrum in a superconductor using a STM. We have measured electron tunneling *I-V* characteristics for NbN and Pb. We have observed variations in the superconductor energy gap in *I-V* measurements of Pb thin films. One possible explanation for this observation is gap anisotropy observed for Pb combined with the polycrystalline nature of the deposited films and the local nature of the STM tunnel probe. In addition, our *I-V* measurements on NbN and Pb films under typical STM conditions showed no evidence for multiparticle tunneling effects.

This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, as part of the Center for Space Microelectronics Technology and was sponsored by the Strategic Defence Initiative Organization/Innovative Science and Technology through an agreement with the National Aeronautics and Space Administration (NASA).

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